Ideal Gas Thermodynamic Properties of Propyl *tert*-Butyl Ethers from Density Functional Theory Results Combined with Experimental Data[1]

O. V. Dorofeeva,[2,3] V. S. Yungman,[2] R. M. Varushchenko,[4] and A. I. Druzhinina[4]

Ideal gas thermodynamic properties, $S^\circ(T)$, $C_p^\circ(T)$, $H^\circ(T)-H^\circ(0)$, $\Delta_f H^\circ(T)$, and $\Delta_f G^\circ(T)$, are obtained on the basis of density functional B3LYP/6-31G(d,p) and B3LYP/6-311+G(3df,2p) calculations for two propyl *tert*-butyl ethers. All torsional motions about C–C and C–O bonds were treated as hindered internal rotations using the independent-rotor model. The empirical approximation was assumed to account for the effect of the coupling of rotor potentials. The correction for rotor-rotor coupling was found by fitting to the entropy values determined from calorimetric measurements. Enthalpies of formation were calculated using isodesmic reactions.

KEY WORDS: calorimetric measurements; DFT calculations; ideal gas; propyl *tert*-butyl ethers; thermodynamic properties.

1. INTRODUCTION

Ethers have been and are becoming more and more an interesting class of reactants and products in the science of combustion and its application. At the present time the chemical behavior of ethers as fuels and fuel additives is studied extensively. Detailed knowledge of their thermodynamics is important in modeling of complicated reaction system, such as combustion and atmospheric oxidation processes.

In this work the ideal gas thermodynamic properties of *n*-propyl *tert*-butyl ether (NPTBE) and isopropyl *tert*-butyl ether (IPTBE) were obtained on the basis of density functional theory (DFT) calculations which have been successfully applied to a variety of organic compounds [1-4]. Unfortunately, now it is not possible to obtain the accurate thermodynamic properties of NPTBE and IPTBE from theoretical calculations only. These molecules have seven internal rotations and the rigorous treatment requires a full analysis of rotor-rotor coupling, whereas a multi-dimensional model for calculating the energy levels of internal rotation has not yet developed for such complicated cases. Hence we used an independent-rotor approximation and the empirical correction was employed to account for the interaction between rotating groups. This correction was determined from comparison of calculated and experimental entropy values.

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[2] Glushko Thermocenter, Institute for High Energy Densities, Associated Institute for High Temperatures, Russian Academy of Sciences, Izhorskaya St. 13/19, Moscow 125412, Russia.

[3] To whom correspondence should be addressed. E-mail: olga.d@ru.net

[4] Department of Chemistry, Moscow State University, Moscow 119992, Russia.

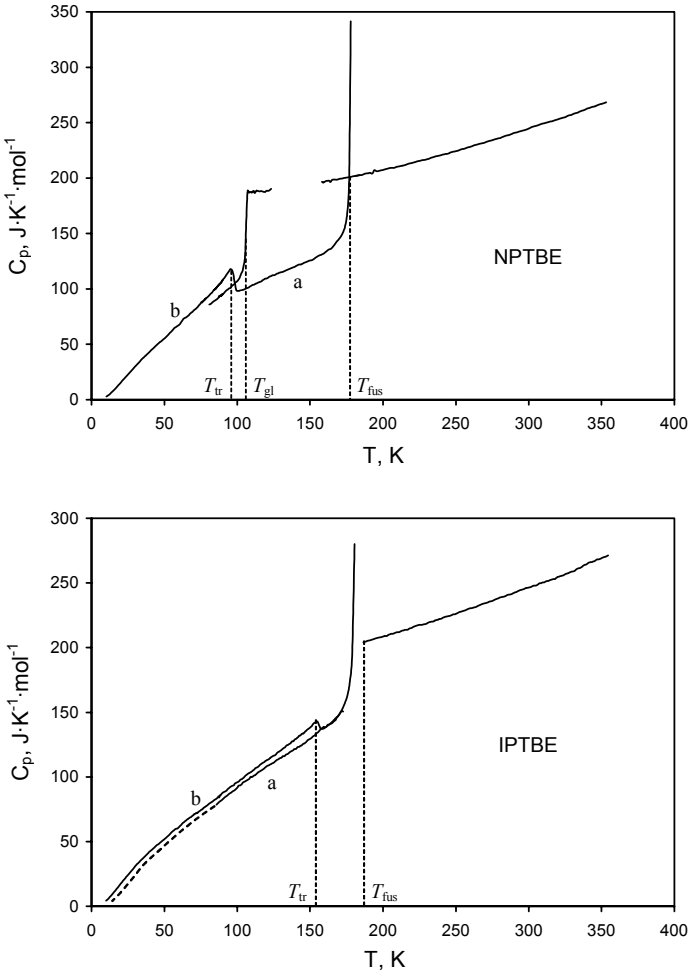


Fig. 1. Heat capacities of NPTBE and IPTBE as a function of temperature: (a) stable and (b) metastable polymorphs.

2. EXPERIMENTAL RESULTS

The heat capacity of two ethers was measured in the temperature range 10 – 353 K using the automated vacuum adiabatic calorimeter. The unit consists of a minicryostat with a calorimeter and an Aksamit system for controlling the heat capacity measurements and collecting and processing experimental data [5]. Temperature was measured by an iron-rhodium resistance thermometer (R ~ 100 Ω) accurate to ≤ $1 \cdot 10^{-2}$ K. The volume of the container for substances was ~ 1 cm^3. The errors of the heat capacity measurements are 1.5 – 2 % at temperatures below 10 K, 0.5 – 1.0 % at 10 – 80 K, and 0.1 – 0.3 % above 80 K.

In the temperature range studied, IPTBE exists in the liquid state as metastable (Fig. 1, b) and stable polymorphs (Fig. 1, a) [6]. The heat capacity curve of NPTBE [6] reveals the metastable (Fig.1, b) and stable (Fig. 1, a) polymorphs and a vitreous and liquid states.

Table I. Thermodynamic Properties of NPTBE and IPTBE

	NPTBE	IPTBE
T_{fus}, K	179.6 ± 0.1	184.78 ± 0.05
$\Delta_{fus}H_m$, kJ·mol^{-1}	9.87 ± 0.08	8.460 ± 0.002
$\Delta_{fus}S_m$, J·K^{-1}·mol^{-1}	55.0 ± 0.4	45.78 ± 0.01
T_{tr}, K	98.3	155.1
T_{gl}, K	107.2	–
$C_{p,m}$(298.15) (l), J·K^{-1}·mol^{-1}	244.00 ± 0.49	245.74 ± 0.49
$\Delta_v H_m^\circ$ (298.15), kJ·mol^{-1}	36.57 ± 0.20	34.48 ± 0.19
$\Delta_v S_m^\circ$ (298.15), J·K^{-1}·mol^{-1}	122.66 ± 0.67	115.65 ± 0.67
Rln[p(298.15)/101325 Pa]	-23.28	-19.50
$\{S_m^\circ(298.15\ \text{K}) - S_m^\circ(0)\}$ (l), J·K^{-1}·mol^{-1}	330.25 ± 0.62	310.31 ± 0.68
$\{H_m^\circ(298.15\ \text{K}) - H_m^\circ(0)\}$ (l), kJ·mol^{-1}	51.18 ± 0.10	49.06 ± 0.11
$\{S_m^\circ(298.15\ \text{K}) - S_m^\circ(0)\}$ (g), J·K^{-1}·mol^{-1}	429.6 ± 0.9	406.4 ± 0.9

The purity of the ethers was determined by calorimetric fractional melting study and was 99.11 and 99.45 mol. %, respectively. Table I lists the temperatures of fusion, T_{fus}, transitions, T_{tr}, and vitrification, T_{gl}, and enthalpies of fusion, $\Delta_{fus}H_m$, and entropies of fusion, $\Delta_{fus}S_m$.

The heat capacity of crystalline ethers was extrapolated from 10 K to T→0 with accuracy of ~ 3 % by the equation:

$$C_{p,m} = \alpha T^3 + \gamma T$$

The thermodynamic functions of the ethers (Table I) were calculated by integrating the $C_{p,m} = f(T)$ dependences for crystalline and liquid phases and adding the enthalpies and entropies of fusion and vaporization and entropy of ideal gas compression obtained from the vapor pressure data [7]. The enthalpies and entropies of vaporization were measured by calorimetric method at 298.15 K [7].

3. THEORETICAL CALCULATIONS

3.1. Methods of Calculations

The DFT calculations were performed using the Gaussian 98 software package [8]. The structural parameters were fully optimized at the B3LYP/6-31G(d,p) level. Vibrational frequencies, zero-point energies, and thermal corrections were calculated at the same level. The scaling factors of 0.958 and 0.975 were applied to C–H stretchings and to all other frequencies, respectively. These values were obtained from fitting the experimental vibrational fundamentals of some ethers.

Potential functions for internal rotation about C–C and C–O bonds were determined by scanning the torsional angles from 0° to 360° at 15° increments and allowing all other structural parameters to be optimized at the B3LYP/6-31G(d,p) level. The potential energy function thus obtained was then fitted to the Fourier series

$$V(\varphi) = V_0 + \frac{1}{2}\sum_n V_n(1-\cos n\varphi) + \frac{1}{2}\sum_n V_n'(1-\sin n\varphi) \qquad (1)$$

The values of $S^\circ(T)$, $C_p^\circ(T)$, and $H^\circ(T) - H^\circ(0)$ were calculated by standard statistical thermodynamic formulae using the rigid-rotor harmonic-oscillator approximation with correction for internal rotation. Internal rotational contributions for each rotor were calculated by direct summation over the energy levels, which were obtained by the diagonalization of the one-dimensional Hamiltonian with fitted torsional potential (Eq. 1). The method for generating the internal rotational energy levels has been described by Lewis et al. [9, 10].

Enthalpies of formation were calculated at the B3LYP/6-311+G(3df,2p)// B3LYP/6-31G(d,p) level using the isodesmic reactions. An isodesmic reaction is one in which the number of bonds of each type is conserved on the two sides of the reaction, and then one might expect the cancellation of errors arising from insufficient treatment of electron correlation and incompleteness of the basis sets. In recent years the method of isodesmic reactions has been employed to evaluate the $\Delta_f H_{298}^\circ$ values of different molecules [11-16].

3.2. Enthalpies of Formation

From analysis of available experimental data, rather different values were reported for the enthalpy of formation of IPTBE: –358.1 ± 3.0 kJ·mol^{-1} [17] and –342.3 kJ·mol^{-1} [18]. Based on five isodesmic reactions given in Table II, the value of

$$\Delta_f H_{298}^\circ(\text{ IPTBE, 298.15 K, gas}) = -349 \pm 5 \text{ kJ·mol}^{-1}$$

was obtained in this work. Note, that in addition to being isodesmic, the reactions 2 and 4 are the homodesmotic reactions [12]. Not only bond types are conserved in these reactions, but also the environment in which these bonds are located. Due to closer matching of bonding environments in reactants and products, as compared to isodesmic reaction, the homodesmotic reaction gives more accurate estimates of the $\Delta_f H_{298}^\circ$ values.

Seven homodesmotic reactions were selected to determine the enthalpy of formation of NPTBE (Table II). The values in Table II are related to the most stable TG conformer. A correction for the mixture of TG and TT conformers (0.2 kJ·mol^{-1}) was estimated from the conformational energy differences based on Boltzmann averaging. Thus, the value of

$$\Delta_f H_{298}^\circ(\text{ NPTBE, 298.15 K, gas}) = -339 \pm 3 \text{ kJ·mol}^{-1}.$$

was accepted in this work. This value is in close agreement with value of –339.3 ± 2.1 kJ·mol^{-1}, calculated from the experimental enthalpy of reaction [18]. It should be noted that

Table II. Enthalpies of Reaction and Enthalpies of Formation for NPTBE and IPTBE Calculated at B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) Level from Isodesmic Reactions

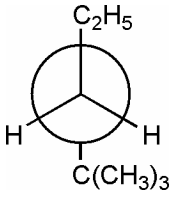
No.	Isodesmic reaction [a]	$\Delta_r H^\circ_{298}$	$\Delta_f H^\circ_{298}$
	Isopropyl *tert*-butyl ether (IPTBE)		
1	$(CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3 = (CH_3)_2CH\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$	-0.1	-349.0
2	$(CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_3 = CH_3\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + (CH_3)_2CH\text{-}O\text{-}CH_3$	-2.4	-347.1
3	$(CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3 = (CH_3)_2CH\text{-}O\text{-}CH(CH_3)_2 + CH_3\text{-}O\text{-}C(CH_3)_3$	2.7	-353.5
4	$(CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + (CH_3)_2CH\text{-}O\text{-}CH_3 = (CH_3)_2CH\text{-}O\text{-}CH(CH_3)_2 + CH_3\text{-}O\text{-}C(CH_3)_3$	-3.1	-347.8
5	$(CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + (CH_3)_2CH\text{-}O\text{-}CH_3 = CH_3\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}C(CH_3)_3$	3.5	-349.1
		average	-349.3
	n-Propyl *tert*-butyl ether (NPTBE)		
6	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_3 = CH_3\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$	0.8	-338.5
7	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_3 = CH_3\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_3\text{-}CH_2\text{-}CH_3$	1.4	-340.7
8	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3 = CH_3\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$	1.6	-340.2
9	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_3 = CH_3\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$	2.4	-338.0
10	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3 = CH_3\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$	2.5	-336.3
11	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3 = CH_3\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$	2.6	-337.5
12	$CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}O\text{-}CH(CH_3)_2 = (CH_3)_2CH\text{-}O\text{-}C(CH_3)_3 + CH_3\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_3$	4.8	-340.2
		average	-338.8

[a] The experimental values of $\Delta_f H^\circ_{298}$ for species used in the isodesmic reactions were taken from Pedley [17], except for IPTBE, reaction 12 (see text).

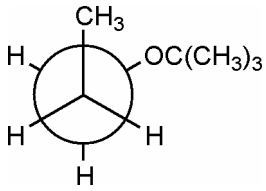
IPTBE with calculated above value of $\Delta_f H^\circ_{298}$ = –349 kJ·mol^{-1} is used as a reference molecule in reaction 12. Using the experimental $\Delta_f H^\circ_{298}$ values for IPTBE [17, 18] leads to significant difference between enthalpies of formation of NPTBE calculated from reaction 12 and reactions 6–11. This is an additional evidence in support of $\Delta_f H^\circ_{298}$(IPTBE) value calculated in this work.

3.3. Geometry, Vibrational Frequencies, and Torsional Potentials

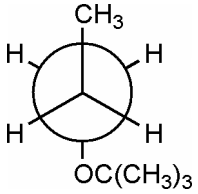
The DFT calculations predict the existence of two stable low energy conformers of NPTBE: *trans-gauche* (TG) conformer of C_1 symmetry is only 0.8 kJ·mol^{-1}(67 cm^{-1}) more stable than *trans-trans* (TT) conformer of C_s symmetry. Both conformers have *trans* location of bulky groups relative to the C–O bond [$CH_3CH_2CH_2$–$OC(CH_3)_3$]



and different relative positions of bulky groups around the C–C bond [CH_3CH_2–$CH_2OC(CH_3)_3$]:



TG



TT

Calculated potential energy curves as a function of torsion angles φ(C–O) and φ(C–C) are shown in Fig. 2. For rotation about the C–C bond, the minima on the potential curve at 0° and 120° correspond to the TT and TG conformers, respectively. Moments of inertia for optimized TG geometry, vibrational frequencies, and coefficients V_n in the expansion for the torsional potentials (Eq. 1) are given in Table III. We did not take into account the difference between geometry and vibrational frequencies of TG and TT conformers of NPTBE because this results in insignificant changes of $S^\circ(T)$ and $C_p^\circ(T)$ values (0.2 and 0.5 J·K^{-1}·mol^{-1}, respectively, at 298.15 K). The energy of next stable conformer of NPTBE, *gauche-trans* (GT), is 14 kJ·mol^{-1} (1150 cm^{-1}) higher than that of TG conformer. Since the GT conformer makes negligible contribution to the thermodynamic functions, we ignored it in thermodynamic functions calculation.

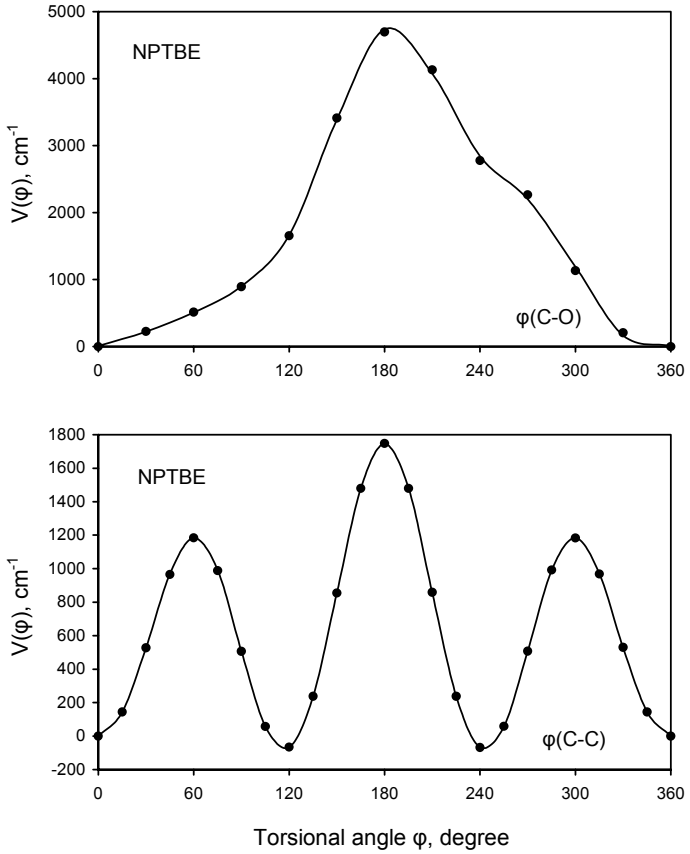
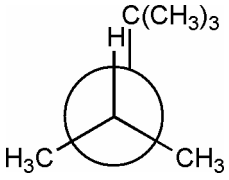


Fig. 2. Torsional potential functions of NPTBE. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Lines are Fourier expansion with the coefficients listed in Table III.

In IPTBE molecule, the branched groups lie on each side of the oxygen atom and nonbonded interactions result in single stable low energy *eclipsed* conformer of C_s symmetry:



The potential energy curve as a function of φ(C–O) torsional angle [$(CH_3)_2CH–OC(CH_3)_3$] is shown in Fig. 3. The minima on the potential curve at 0° and ~165° correspond to the

Table III. Moments of Inertia, Vibrational Frequencies and Internal Rotational Molecular Constants of NPTBE and IPTBE Calculated at B3LYP/6-31G(d,p) Level

NPTBE: TG conformer

Point group: C_1	I_A=25.1031×10^{-39} g·cm^{-1}
Symmetry number: σ=1	I_B=77.2003×10^{-39} g·cm^{-1}
Ground electronic state: $\tilde{X}\,^1A$	I_C=81.1320×10^{-39} g·cm^{-1}
Molecular weight: 116.2028	$I_AI_BI_C$=157231×10^{-117} g^3·cm^6

Vibrational frequencies:[a] 3004, 3000, 3000, 2994, 2992, 2989, 2985, 2978, 2948, 2926, 2919, 2918, 2915, 2912, 2890, 2859, 1502, 1492, 1487, 1477, 1476, 1471, 1464, 1461, 1456, 1450, 1401, 1396, 1384, 1373, 1370, 1351, 1285, 1249, 1245, 1228, 1203, 1150, 1117, 1078, 1025, 1017, 1003, 937, 913, 901, 890, 870, 868, 766, 716, 506, 458, 445, 385, 337, 331, 290, 264,[b] 254,[b] 232,[b] 207,[b] 166,[b] 144, 80,[b] 21[b]

[a] Scaling factor of 0.958 was used for C–H stretchings and 0.975 for other modes.

[b] Instead of these torsional modes, the contributions due to the internal rotation were calculated from the potential (Eq. 1).

CH_3 group: I_r=0.5200×10^{-39} g·cm^{-1}, σ_m=3, V_3=1127 cm^{-1},
CH_3 group: I_r=0.5212×10^{-39} g·cm^{-1}, σ_m=3, V_3=1107 cm^{-1},
CH_3 group: I_r=0.5203×10^{-39} g·cm^{-1}, σ_m=3, V_3=1002 cm^{-1},
CH_3 group: I_r=0.5229×10^{-39} g·cm^{-1}, σ_m=3, V_3=1163 cm^{-1},
C_2H_5 group: I_r=3.6882×10^{-39} g·cm^{-1}, σ_m=1, V_1=355.5, V_2= – 333.0, V_3=1414.7, V_4= – 86.6, V_5= – 24.7, V_6= – 32.5 (in cm^{-1}),
t-C_4H_9 group: I_r=5.2310×10^{-39} g·cm^{-1}, σ_m=3, V_3=973 cm^{-1},
C_3H_7 group: I_r=7.0462×10^{-39} g·cm^{-1}, σ_m=1, V_0= – 201.2, V_1=4085.7, V_2= – 824.6, V_3=640.3, V_4= – 272.6, V_1'=1075.6, V_2'= – 357.9, V_3'= – 224.0, V_4'= – 69.2 (in cm^{-1}).

IPTBE: *eclipsed* conformer

Point group: C_s	I_A=28.8592×10^{-39} g·cm^{-1}
Symmetry number: σ=1	I_B=62.3435×10^{-39} g·cm^{-1}
Ground electronic state: $\tilde{X}\,^1A'$	I_C=70.4758×10^{-39} g·cm^{-1}
Molecular weight: 116.2028	$I_AI_BI_C$=126799×10^{-117} g^3·cm^6

Vibrational frequencies:[c] *A′* 3000, 2999, 2994, 2990, 2987, 2926, 2920, 2919, 2906, 1494, 1484, 1478, 1472, 1463, 1401, 1393, 1378, 1356, 1251, 1204, 1175, 1119, 1028, 1012, 902, 871, 809, 720, 508, 461, 404, 346, 291, 266,[d] 250,[d] 185, *A″* 3001, 2996, 2993, 2982, 2982, 2916, 2914, 1476, 1464, 1460, 1456, 1449, 1378, 1373, 1330, 1226, 1127, 1021, 939, 919, 906, 887, 467, 388, 311, 259,[d] 216,[d] 199,[d] 84,[d] 37[d]

[c] Scaling factor of 0.958 was used for C–H stretchings and 0.975 for other modes.

[d] Instead of these torsional modes, the contributions due to the internal rotation were calculated from the potential (Eq. 1).

CH_3 groups (2): I_r=0.5209×10^{-39} g·cm^{-1}, σ_m=3, V_3=1109 cm^{-1},
CH_3 groups (2): I_r=0.5204×10^{-39} g·cm^{-1}, σ_m=3, V_3=1217 cm^{-1},
CH_3 group: I_r=0.5214×10^{-39} g·cm^{-1}, σ_m=3, V_3=1166 cm^{-1},
t-C_4H_9 group: I_r=7.6445×10^{-39} g·cm^{-1}, σ_m=3, V_3=985 cm^{-1},
i-C_3H_7 group: I_r=6.8367×10^{-39} g·cm^{-1}, σ_m=1, V_1=2557.0, V_2=908.1, V_3= – 695.8, V_4=141.6, V_5=264.4, V_6= – 59.4 (in cm^{-1}).

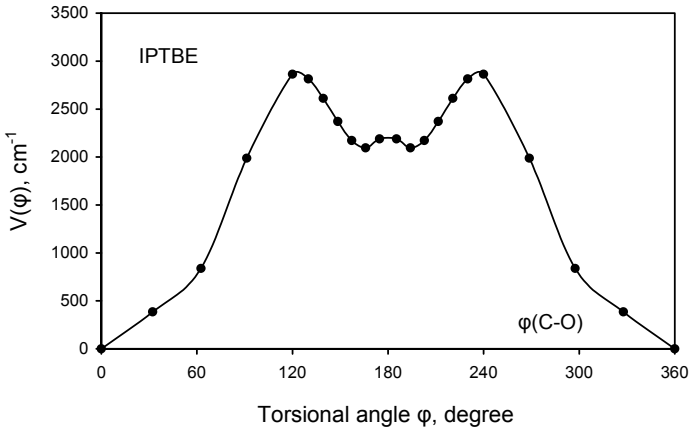


Fig. 3. Torsional potential function of IPTBE. Points are calculated values at the B3LYP/6-31G(d,p) level of theory. Lines are Fourier expansion with the coefficients listed in Table III.

eclipsed and near-*trans* conformers, respectively. The energy of the near-*trans* conformer is 25 kJ·mol^{-1} (2090 cm^{-1}) higher than that of *eclipsed* conformer. Calculated molecular parameters of IPTBE are given in Table III.

3.4. Thermodynamic Functions

Thermodynamic functions, $S^\circ(T)$, $C_p^\circ(T)$, and $H^\circ(T) - H^\circ(0)$, were calculated within the framework of the rigid-rotor harmonic-oscillator approximation for all rotation and vibration modes, except for internal rotation modes for which the independent-rotor model was employed. This model results in the overestimated values of thermodynamic functions as compared with $S^\circ(T)$ and $C_p^\circ(T)$ values determined from calorimetric measurements for alkyl ethers (Table IV). The greater is the number of rotors, the greater the discrepancies between calculated and experimental values. Especially large discrepancies are found for *tert*-alkyl ethers. It is most likely that the increased error is associated with the independent-rotor assumption.

To our knowledge, the theoretical models for computing the internal rotational contributions for species with three and more rotors have not been devised. Chen et al. [19] failed to reproduce the observed heat capacities and entropy of isobutane by assuming independent methyl rotation with any value of V_3. The authors [19] concluded that interaction among methyl groups has a significant effect on thermodynamic functions. The rotor-rotor interactions in isobutane were approximated by the potential parameter V_6 which was determined empirically by comparison with experimental values of $S^\circ(T)$ and $C_p^\circ(T)$.

Table IV. Deviation of Entropies and Heat Capacities of Ethers Calculated by B3LYP/6-31G(d,p) Method from Experiment (in $J \cdot K^{-1} \cdot mol^{-1}$)

	exp – calc			exp – calc	
$CH_3–CH_2–O–CH_2–CH_3$ [a]			$CH_3–O–C(CH_3)_3$ [b]		
	no correction	corrected ($K_{r\text{-}r}$=0.964)		no correction	corrected ($K_{r\text{-}r}$=0.892)
S°(342.31)	-1.7	0.4	S°(298.15)	-5.9	0.0
C_p°(309.98)	-2.1	-0.4			
C_p°(350.00)	-1.9	-0.3			
C_p°(400.04)	-1.5	0.1			
C_p°(450.04)	-1.0	0.5			
$CH_3–CH_2–CH_2–O–CH_2–CH_2–CH_3$ [c]			$(CH_3)_2CH–O–CH(CH_3)_2$ [d]		
	no correction	corrected ($K_{r\text{-}r}$=0.923)		no correction	corrected ($K_{r\text{-}r}$=0.922)
S°(298.15)	-9.8	-1.1	S°(298.15)	-7.0	-0.2
C_p°(360.00)	-4.0	0.8	S°(340.00)	-7.7	-0.4
C_p°(380.01)	-4.0	0.8	C_p°(360.04)	-4.6	-0.4
C_p°(399.98)	-3.9	0.8	C_p°(380.01)	-4.3	-0.1
C_p°(430.05)	-3.7	0.9	C_p°(399.98)	-4.1	0.2
C_p°(460.01)	-3.3	1.2	C_p°(449.98)	-3.6	0.7
$CH_3–CH_2–CH_2–O–C(CH_3)_3$ [e]			$(CH_3)_2CH–O–C(CH_3)_3$ [e]		
	no correction	corrected ($K_{r\text{-}r}$=0.867)		no correction	corrected ($K_{r\text{-}r}$=0.774)
S°(298.15)	-14.3	-0.4	S°(298.15)	-20.4	-0.8
S°(313.15)	-13.6	0.6	S°(313.15)	-20.7	-0.4
S°(323.15)	-14.4	0.1	S°(323.15)	-20.7	0.1
S°(333.15)	-14.8	0.0	S°(333.15)	-20.7	0.5
S°(343.15)	-14.9	0.2	S°(343.15)	-20.7	0.9
S°(353.15)	-14.8	0.5	S°(353.15)	-20.7	1.3

Experimental data were taken from: [a] Ref. 20. [b] Ref. 21. [c] Ref. 22. [d] Ref. 23. [e] This work; for 298.15 K the entropies of vaporization were calculated using enthalpies of vaporization measured by calorimetric method at 298.15 K [7]; for other temperatures the entropies of vaporization were calculated from the vapor pressure data [7].

Table V. Ideal Gas Thermodynamic Properties of NPTBE and IPTBE ($p°$=101.325 kPa)

T (K)	C_p° (J·K^{-1}·mol^{-1})	S° (J·K^{-1}·mol^{-1})	$-[G^\circ - H^\circ(0)]/T$ (J·K^{-1}·mol^{-1})	$H^\circ - H^\circ(0)$ (kJ·mol^{-1})	$\Delta_f H^\circ$ (kJ·mol^{-1})	$\Delta_f G^\circ$ (kJ·mol^{-1})
			NPTBE			
0	0.0	0.0	∞	0.0	-291.0	-291.0
150	108.1	335.1	265.5	10.4	-318.8	-219.2
200	130.7	369.3	287.2	16.4	-325.8	-184.9
250	154.0	400.9	306.8	23.5	-332.6	-148.9
298.15	177.2	430.0	324.4	31.5	-339.0	-113.0
300	178.1	431.1	325.0	31.8	-339.2	-111.6
350	202.1	460.4	342.3	41.3	-345.4	-73.1
400	225.3	488.9	358.8	52.0	-350.9	-33.8
500	267.0	543.8	390.4	76.7	-360.5	46.6
600	302.4	595.7	420.3	105.2	-368.0	128.7
700	332.3	644.6	448.9	137.0	-373.8	212.0
800	358.1	690.7	476.3	171.5	-377.9	295.9
900	380.3	734.2	502.6	208.5	-380.7	380.4
1000	399.6	775.3	527.8	247.5	-382.4	465.0
			IPTBE			
0	0.0	0.0	∞	0.0	-299.6	-299.6
150	102.6	314.5	251.5	9.4	-328.4	-225.7
200	127.4	347.4	271.4	15.2	-335.6	-190.3
250	151.8	378.5	289.7	22.2	-342.6	-153.2
298.15	175.4	407.2	306.4	30.1	-349.0	-116.2
300	176.3	408.3	307.0	30.4	-349.2	-114.7
350	200.6	437.3	323.6	39.8	-355.4	-75.1
400	223.8	465.6	339.6	50.4	-361.1	-34.7
450	245.5	493.3	355.1	62.2	-366.2	6.4
500	265.5	520.2	370.3	74.9	-370.8	48.1
600	300.8	571.8	399.6	103.3	-378.5	132.6
700	330.7	620.5	427.7	134.9	-384.4	218.2
800	356.4	666.4	454.7	169.3	-388.7	304.6
900	378.5	709.6	480.7	206.1	-391.7	391.5
1000	397.6	750.5	505.6	244.9	-393.5	478.6

In this work the contribution to the thermodynamic functions due to coupling of rotor potentials was taken into account by multiplying the partition function for uncoupling internal rotations by empirical factor $K_{r\text{-}r}$. The $K_{r\text{-}r}$ values of 0.867 and 0.774 were found by fitting to the experimental entropies of NPTBE and IPTBE, respectively. The difference between experimental and thus calculated entropies is shown in Table IV. It should be noted that the employed procedure for correction of the thermodynamic functions does not violate well-known thermodynamic relation between calculated values of $S^\circ(T)$, $C_p^\circ(T)$, and $H^\circ(T) - H^\circ(0)$.

Table V lists the thermodynamic properties of NPTBE and IPTBE calculated using molecular constants (Table III) and enthalpies of formation (see Section 3.2) estimated in this work. Since the calculated entropy values were fitted to the experimental ones, their uncertainty is close to the uncertainty of experimental values. A comparison of trends in heat capacity values for alkanes and ethers shows that calculated $C_p^\circ(T)$ values for NPTBE and IPTBE agree with correlations utilized empirical group additivity contributions. The uncertainty of calculated $C_p^\circ(T)$ values is estimated to be 5-8 $J \cdot K^{-1} \cdot mol^{-1}$.

4. CONCLUSION

Thermodynamic properties of NPTBE and IPTBE were obtained by combining the DFT results with experimental $S^\circ(T)$ values determined from calorimetric investigations. The preliminary calculations for other alkyl ethers suggest that there is a trend in empirical corrections for the rotor-rotor coupling. We believe that further calculations for ethers allow us to estimate the missing groups and to develop a group additivity scheme for accurate estimation of thermodynamic properties of alkyl ethers.

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